

Proton Nuclear Magnetic Resonance (NMR) Relaxometry in Soil Science Applications

Julia V. Bayer*, Fabian Jaeger and Gabriele E. Schaumann

Department of Environmental and Soil Chemistry, Institute of Environmental Sciences, University of Koblenz-Landau, Fortstraße 7, 76829 Landau, Germany

Abstract: Proton NMR relaxometry is a very powerful tool for investigating porous media and their interaction with water or other liquids and the mobility and interaction of organic molecules in solution. It is commonly used in material science or earth science. However, it is only scarcely applied in soil science although it shows great potential for helping to understand water uptake into the soil matrix and processes occurring at the solid-liquid interface at soil particle surfaces. This review introduces proton NMR relaxometry in the context of soil science and discusses the most important applications of the method in this field. Relevant results from different applications of NMR relaxometry in soils are described and research gaps identified. Some original data is presented concerning biofilm formation in soils, which was investigated using proton NMR relaxometry. NMR relaxometry is a sensitive, informative and promising method to study pore size distribution in soils as well as many kinds of soil physicochemical processes, among which are wetting, swelling or changes in macromolecular status. It is further a very helpful method to study interactions between molecules in soil organic matter and can serve to study the state of binding of water or organic chemicals to soil organic matter. Relaxation times determined by NMR relaxometry are sensitive to various factors that play a role in soil-water interaction which is both an advantage and shortcoming of the method: NMR relaxometry can be applied to numerous investigations in soil science, but at the same time interpretation of the results may be very difficult in such complex and heterogeneous systems like soils.

Keywords: NMR relaxometry, soil, porous media, water, swelling, wetting.

INTRODUCTION

Proton NMR relaxometry is commonly used in geosciences, e.g. in oil exploration, and material sciences [1, 2]. It is a powerful tool for non-destructive investigations of pore size distributions of porous media, water content, water uptake and re-distribution as well as molecule mobility and non-covalent binding mechanisms. The technique can be adapted for use in soil investigations, but so far has only been used sparsely. More frequently used for structural analysis is NMR spectroscopy which is able to give insight into the molecular structure of soil organic matter (SOM). It has been used extensively for the determination of humic acid (HA) and fulvic acid (FA) structures and other organic constituents in SOM in either liquid or solid state. Detailed reviews of the state of the art of NMR spectroscopy in natural organic matter NOM, heterogeneous material and polymers are given elsewhere [3-5]. More specific details of NMR spectroscopy applications in soil, SOM and biological systems, including several other NMR techniques like magnetic resonance imaging (MRI) and the investigation of mobility of deuterated or fluorinated compounds, can be found e.g. in [6-11].

This review focuses mainly on the application of proton NMR relaxometry in soil science, especially ^1H NMR

relaxometry, including some relevant studies on other porous media and magnetic resonance imaging (MRI) studies of soils. Unfortunately, NMR relaxometry as used for studies in geosciences cannot be transferred one to one for studying soils, as e.g. the pore system differs from that found in rock formations. The main challenge for application to soil is, in this context, its huge complexity and heterogeneity and the up to now only scarcely understood soil organic matter [12, 13]. Nevertheless, efforts have been made to use NMR relaxometry to describe pore size distributions in soils, as well as processes occurring during water uptake, i.e. wetting, swelling of organic matter and re-distribution of water.

Apart from pure NMR relaxometry, MRI studies, based on the same measurement principle as NMR relaxometry, may help to get insight into soil water interactions as they provide spatial resolution additional to the temporal resolution. Many studies employ MRI for understanding water uptake into soils or similar porous media and gain qualitative and quantitative information about local water distribution: Theoretical considerations about formation of preferential flow pathways have been confirmed by MRI; water and hydrocarbon distribution and displacement have been evaluated and water distribution within the pore system can be observed, e.g. [14-22]. However, the resolution of MRI is much lower than that of NMR relaxometry and no detailed information about the pore size distribution or water properties within the pores can be determined from such measurements. Apart from ^1H NMR relaxometry, other nuclei such as ^{13}C or ^{19}F can be used for relaxation studies of liquids in porous media giving insight into distribution of those liquids [23,

*Address correspondence to this author at the Department of Environmental and Soil Chemistry, Institute of Environmental Sciences, University of Koblenz-Landau, Fortstraße 7, 76829 Landau, Germany; Tel: +49 (0)6341-280-565; Fax: +49 (0)6341-280-576; E-mail: bayer@uni-landau.de

24] and the pore size distribution of the porous media, e.g. [25, 26].

Gaining insight into water distribution in soils is especially important for nutrient and contaminant distribution, which is of interest for agricultural applications and in relation to aquifer contamination [27]. Any substance entering the soil pore system interacts with the solid surface and, therefore, depends on solution distribution and interaction with the matrix. Water uptake in soils is not a simple distribution problem as e.g. preferential pathways form due to the existence of macropores and different surface wettabilities of the solid surface influence the wetting process [28]. Also, water does not only enter pores, but interacts with the organic matter coatings and organic colloids present in the pore system. This changes the solid surface and, hence, the pore system itself. Model calculations are often inadequate in describing water uptake into and the interaction of water with the soil matrix [27, 28]. NMR relaxometry, therefore, offers a great potential for investigating soil water interactions without the need for modelling or sample destruction. The method can be used *in-situ*, especially with more recent developments in mobile NMR techniques that could be used directly in the field [29-37].

Addressing both soil scientists interested in the use of these techniques for their own purpose and NMR specialists providing new promising NMR relaxometry tools which help to obtain further insights into soil processes, the objective of this contribution is to outline and discuss fields of application of this technique in soil science. Although, different NMR methods are commonly used in soil science applications, this review focuses mainly on proton NMR relaxometry, due to the complexity of the field.

BASICS OF NMR RELAXOMETRY

This section is addressed mainly to the reader unfamiliar with the field of NMR. Many atomic nuclei possess a non-zero spin and an intrinsic magnetic moment parallel or antiparallel to the spin. The spin is associated with a non-zero magnetic moment (μ) via the relation $\mu = \gamma J$, where γ is the gyromagnetic ratio and J the spin angular momentum. γ is constant, but assumes different values for different nuclei. When placed in an outer magnetic field B (conventionally along the z -axis), the spins orientate and precess about the external field with the Larmor frequency, which is characteristic for each nucleus and dependent on the strength of the outer magnetic field (e.g. hydrogen nucleus 42.6 MHz at 1 Tesla): $f = \gamma B / 2\pi$ (e.g., [1]).

A radio frequency (RF) pulse with the characteristic Larmor frequency is applied and the spins are flipped into an angle to the external magnetic field (B_0) causing a magnetisation (M_0). In most applications the RF pulse turns the spins in 90° or 180° direction (in a certain pulse sequence). After the RF pulse is switched off the spins relax to their equilibrium orientation and the apparent magnetisation induced by the RF pulse decays. The measured signal is called the free induction decay (FID) [2]. The relaxation process generally is a first order process. It is characterized by the relaxation time, which is the reciprocal of the relaxation rate constant. Two different relaxation mechanisms are involved in the

magnetisation decay, which are the *longitudinal* or *spin-lattice* and *transverse* or *spin-spin* relaxation [2].

The spin-lattice relaxation time T_1 depends mainly on the interaction of the spins with their environment often referred to as the lattice, hence the name. T_1 describes how effective interactions between the spin system and the environment are in exchanging magnetic energy. If strong interactions between the spin system and the environment lead to a fast exchange of energy, the equilibrium state is reached fast and T_1 is short. Measuring T_1 can be very time consuming and is, so far, not often used in soil science applications, although it may be the more appropriate measure than T_2 in many cases [1, 2].

The spin-spin relaxation time T_2 normally refers to the relaxation due to variable molecular interactions or diffusion in the slightly inhomogeneous magnetic field. The transversal relaxation process is not based on energy exchange, but originates from a dephasing of the precessing spins, e.g., due to slight differences in Larmor frequency due to local field inhomogeneity [2]. Variations in the magnetic field caused by neighbouring nuclei are stronger in solids than in liquids where spins can move freely and inhomogeneities due to neighbouring spins are small. As the dephasing of the spins can only take place in the presence of a longitudinal magnetisation T_2 can be smaller than or equal to T_1 , but it can never be longer [1].

While bulk liquids lacking additional means of interaction reveal long proton relaxation times in the range of seconds, limitation of mobility can reduce T_2 . Contrary to T_2 , T_1 can be either increased or reduced by a reduction in mobility, depending on the Larmor frequency and the correlation time for the relaxation-relevant interaction [2]. Molecular diffusion in field gradients affects T_2 but not T_1 , because no energy exchange is involved in this relaxation mechanism [38]. The relaxation rate due to diffusion in field gradients is proportional to the diffusion coefficient and the square of local field gradients [2]. The local field gradients increase with increasing external field strength. Therefore, measurements in systems like soils, where local field gradients are the rule, are to be carried out preferentially in low fields up to 10-50 MHz. Field cycling NMR explicitly investigates the field and frequency dependency of T_1 and T_2 at proton Larmor frequencies between 10 kHz and 40 MHz or higher and is, therefore, a promising tool to study dynamic molecular interactions and to distinguish between the molecular effects and effects of local field gradients or sample heterogeneity [39]. In traditional high-resolution NMR spectroscopy, where Larmor frequencies are generally above 250 MHz, large T_1/T_2 ratios are the rule.

Relaxation Times T_1 and T_2 in Porous Systems

With T_1 and T_2 of protons of bulk water in the range of 1-3 seconds, bulk relaxation processes are very slow. If confined in porous media, relaxation is often controlled by solid-fluid-interactions at the surfaces of the pore space. Water molecules diffuse and eventually reach a pore wall surface where there is a finite probability that their spins are relaxed due to interactions with fixed spins, paramagnetic ions or paramagnetic crystal defects. Further transversal relaxation occurs *via* diffusion in local field gradients. The total relaxa-

tion rate is, therefore, the sum of bulk relaxation (B) and surface relaxation (S) and, for T_2 , of relaxation due to diffusion in field gradients [1]:

$$\begin{aligned} \left(\frac{1}{T_1}\right)_{total} &= \left(\frac{1}{T_1}\right)_B + \left(\frac{1}{T_1}\right)_S \\ \left(\frac{1}{T_2}\right)_{total} &= \left(\frac{1}{T_2}\right)_B + \left(\frac{1}{T_2}\right)_S + \left(\frac{1}{T_2}\right)_{diff-FG} \end{aligned} \quad (1)$$

The surface relaxation term contains information of the pore system and is, therefore, further analysed. Relaxation time at the surface is determined by the residence time of the spin at the surface. The longer the residence time the higher the probability for interaction with the surface and, therefore, relaxation. As long as this surface relaxation is slower than the transport of unrelaxed spins to the surface the *fast-diffusion* or *surface-limited* regime [40] is fulfilled. Water molecules can transit the pore several times before being relaxed and the magnetization decay in an individual pore is, therefore, spatially uniform and depends on the surface-to-volume ratio. Surface relaxation is then related to the internal surface area S , internal pore volume V and the surface relaxivity ρ [1] which is strongly influenced by paramagnetic ions on the surface like Mn^{2+} or Fe^{3+} :

$$\text{surface-limited: } \frac{1}{T_{1,2S}} = \rho_{1,2} \frac{S}{V} \approx \rho_{1,2} \frac{\alpha}{r} \quad (2)$$

where r is the pore radius and α is the shape factor (1, 2, 3 for planar, cylindrical and spherical pore geometry) [41].

If, in contrast, the magnetic decay is controlled by the transport of the molecules to the surface the conditions of the *slow-diffusion* or *diffusion-limited* regime [40] are met. This may be the case if pores are large or surface relaxation is strong, e.g., due to the presence of effective paramagnetic centres.

$$\text{diffusion-limited: } \frac{1}{T_{1S}} = \frac{1}{T_{2S}} = D \frac{c}{r^2} \quad (3)$$

where D is the diffusion coefficient and c is a shape-dependent factor. Note that in the case of diffusion limitation T_{1S} and T_{2S} are equal. Relaxation times in the diffusion-limited regime depend on temperature in the same way as the diffusion coefficient. In this case, relaxation times are not spatially uniform, which results in a multiexponential magnetic decay, even within a single pore, and relaxation is additionally dependent on pore shape [1]:

Converting NMR Signals into Relaxation Time Distributions

For data analysis in NMR relaxometry several different algorithms and software is applied. These are, e.g., the software 'WinDXP' from Resonance Instruments (UK) or 'Contin' used by Bruker (USA) [42], which are device specific, or UPEN, a software developed at the University of Bologna [43, 44]. Depending on the chosen program and parameters, the analyses may lead to differently strongly separated peaks in the relaxation distribution. One such parameter is the

weight factor used in WinDXP to account for different signal to noise ratios. An example is given in Fig. (1) for a water repellent soil sample using a weight factor of 0.1 (Fig. 1a) and 20 (Fig. 1b). The differences in peak separation and peak number clearly demonstrate the importance to consider the effect of evaluation parameters on the resulting relaxation time distribution [45]. Samples can only be compared to each other on the basis of comparable evaluation parameters using the same software.

WATER IN SOILS AND PEATS

Water uptake and redistribution in soils as well as interaction of water with SOM is of great importance for, e.g., contaminant sorption or nutrient availability. The availability of water for plants itself is important in agricultural sciences and is determined by the water content, the matric potential (ψ) and the water retention curve of a soil. Hereby, a matric potential of -1.5 MPa is defined as the permanent wilting point where plant growths is limited due to water shortage; a matric potential of -0.03 MPa is defined as the field capacity which is the amount of water held in a soil after excess water was drained due to gravitation [28]. Measurement of water retention curves by standard soil science methods is time consuming and cannot be carried out *in situ*.

A first effort to use low-field NMR relaxometry for analysis of water in soils was made by Prebble and Currie already in 1970 by measuring T_1 (at 2.7 MHz) [46]. They used several sands, soils and a vermiculite as sample material and added different amounts of water. Three states of water in soils were identified: i) At very low water contents water was tightly bound to the clay or sand interface, but no relationship with plant unavailable water was found ($\psi = -1.5$ MPa); ii) with increasing water content the water seemed to be independent of the clay lattice and water content calculations resulted in values close to the real amount of water added and iii) further addition of water lead to an incomplete relaxation during the measurement time indicating the presence of bulk water ($\psi = -0.03$ MPa). The presence of various states of water was confirmed for peat samples by McBrierty *et al.* [47]. In a detailed study using high field NMR relaxometry (300 MHz), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) the binding of water in peat was investigated and up to four different water states were found, with two forms of loosely bound water, bulk water and tightly bound water that did not freeze at temperatures down to 160 K. The loosely bound water froze around 210 K and bulk water at 273 K, indicating also the temperature range above which each water form became mobile. Drying and re-watering of peat samples did shrink and swell the peat matrix and with that changed the amount of loosely bound water, but the amount of strongly surface associated water was similar after each change in moisture status. Non-freezing water was associated with hydration water, i.e. water in a gel like layer at the solid surface or water that chemically interacts with the hydrophilic moieties on the surface [47]. Therefore, the amount of non-freezing water could be an indicator for surface properties. The interactions of water molecules at the surface of particles is responsible for the thickness of the bound water layer or physisorbed water, which can be up to 3 molecular layers. The relaxation rate increases (linearly) with the amount of solid

surface present, as shown for water clay suspensions, due to the relaxivity offered by the solid surface [48].

The relaxation mechanisms at the solid liquid interface are manifold and paramagnetic substances have an important influence. The coverage of only 0.01% with Fe(III) of a silica surface was enough to increase surface relaxivity by an order of magnitude [49]. However, Mn(II) seems to be an even stronger relaxing agent than Fe(III) with a relaxation acceleration effect of up to three times stronger in solutions [50, 51]. The effect of paramagnetic ions on the surface relaxivity seems to be restricted to one atomic layer at the surface of a particle as shown for Mn(II) on calcite particles [50]. Further increase in manganese concentrations in calcite water systems did not increase surface relaxivity further and also Mn(II) inside calcite particles did not contribute to surface relaxivity either [50]. The effect of paramagnetic substances on the relaxation rate was observed to be much stronger when they are adsorbed to the solid surface, due to the restricted molecular motion of the adsorbed species which in turn results in a longer rotational correlation time for the coordinated water molecules. Nevertheless, bulk relaxation is also accelerated in the presence of dissolved paramagnetic ions [49-51]. The relaxation acceleration effect of paramagnetic substances in the bulk solution is dependent on the speciation of the ion [49, 51]. It was suggested that the relaxation acceleration decreases from hexa-aqua complexes to aqua complexes with a reduced number of exchangeable protons to organic-complexed ions to dispersed colloids. Therefore, the acceleration of the bulk relaxation rate in comparison to pure water may give additional information on the ion environment in complex soil solutions [51].

Due to the dependency of the relaxation times on the water binding and distribution NMR relaxometry can be used to describe the water environment: water in small pores or bound water relaxes faster than that in large pores or free water, due to increased accessibility of the solid surface. Gaining information about water uptake and redistribution in soil systems is of high importance, e.g., for agricultural systems or prediction of contaminant distribution. Several studies so far have been carried out investigating water uptake into soils or clays using relaxation time distributions determined by ^1H -NMR relaxometry [45, 47, 52-59]. Relaxation time distributions generally showed three or four separate

peaks representing different water states or water in different pore systems. The boundary conditions vary between publications, but as a general rule one can differentiate between micropores or tightly surface bound water at small relaxation times (e.g. T_2 : below 60 ms, sometimes separated into several peaks), mesopores or loosely bound water at medium relaxation times (e.g. T_2 : 60 – 300 ms) and macropores or bulk water at long relaxation times (e.g. $T_2 > 300$) [47, 52, 60]. Some researchers found several relaxation time peaks at medium relaxation times. The loosely bound water relaxing with these relaxation times was possibly associated with different separate environments that did not allow water exchange at time scales of the relaxation measurements. Over the course of water uptake relaxation time distributions shifted towards smaller relaxation times and peaks at shorter relaxation times increased in size (Fig. 1a and b) [45, 53-55, 60].

The shift of relaxation times towards shorter times indicates water movement into smaller pores, which is contrary to the common model of water imbibition into porous media with hydrophilic pore walls where small pores are filled first due to capillary forces. As an explanation it was suggested that pore walls become increasingly hydrophilic with increasing soil-water contact time [45, 58] or that micropores that initially collapsed upon drying were reformed during water uptake by formation of water-swollen gels [53]. The latter process was referred to as swelling [53]. However, the definition of swelling is not used consistently in other publications.

Generally, the water uptake and re-distribution were found to be separated into fast and slow processes which can last up to weeks. The activation energies calculated for the fast and slow processes by Todoruk *et al.* [53] indicate that they are fundamentally different: The fast process had activation energies of $\sim 42\text{kJ mol}^{-1}$ which is in the upper range of diffusion associated processes. The slow component, however, had activation energies of $> 80\text{kJ mol}^{-1}$ indicating chemical transformations like ester hydrolysis or more complex rearrangements of SOM components [53]. During wetting of a soil the hydrogen bonds of SOM components and mineral surface, which had been formed previously during drying, have to be broken apart in order to restore hydrophilic surface conditions; this process would be slow and

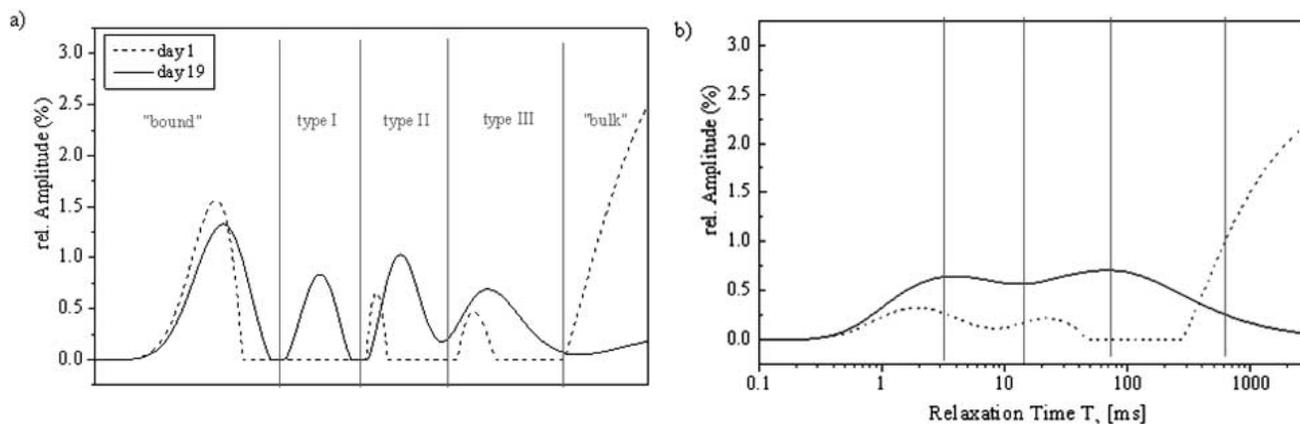


Fig. (1). Comparison of T_2 relaxation time distribution of a water repellent sample directly after water addition and 19 days later using two smoothing values: **a)** weight factor 0.1 and **b)** weight factor 20. Data taken from [45] and adjusted.

energetically unfavourable, leading to high activation energies [53]. Other authors distinguished more clearly between wetting and swelling as two separate more or less independent processes [54]. Wetting was suggested to be considerably faster (indicated by a shorter time constant of relaxation time changes) than swelling in hydrophilic soils and primarily associated with the properties of the solid surface (whether mineral or organic). In order to wet a surface it needs to be hydrophilic, however, prolonged contact of water with an organic hydrophobic soil particle surface could render it wettable and, hence, would allow further processes like swelling to take place. This is displayed in NMR measurements as a slow change in relaxation times towards shorter relaxation times. Swelling here was defined as the hydration of SOM which increases the thickness of the SOM coating or SOM particle. This in turn would lead to a decrease in interparticulate pore size [45, 54]. The process of swelling may be of high relevance for contaminant fixation in soils as it may influence interactions of contaminants with SOM by e.g. increasing the available sorption site, forming new sorption domains or changing its rigidity [54, 61].

As described above it is necessary to have a hydrophilic surface in order to enable instant wetting. However, in systems like soil, surfaces change when in contact with water and originally hydrophobic surfaces become wettable after prolonged contact with water. The breakdown of a hydrophobic surface during wetting is thought to be fast in comparison to swelling. It was suggested to exploit that fact and use low-field ^1H -NMR relaxometry for soil wettability determinations [56, 57, 62]. In order for a liquid in porous media to be relaxed efficiently it needs to be in contact with the solid surface. Theoretical considerations suggest that relaxation times of hydrophobic samples are longer than that of wettable samples enabling a better proton exchange [56, 57]. T_2 of water repellent soil samples and model systems was found to be larger than 1000 ms, but that of wettable samples ~ 100 ms [56, 57]. As described above water repellency of organic coatings on particle surfaces normally breaks down after contact with water, therefore, relaxation times of water repellent and wettable sample should eventually reach the same equilibrium. The decrease of relaxation time and approach of a similar equilibrium was confirmed in two studies and the time for reaching the equilibrium was dependent on the sample [56, 57].

Proton NMR relaxometry studies of water in soil systems allow to distinguish processes taking place during water uptake. It is also possible to differentiate between water in several environments, i.e., bound, loosely bound and free bulk water. Furthermore, influences of factors like paramagnetic substances in solution and on the solid surface have been characterised and partly quantified. However, it is still necessary to quantitatively describe the processes occurring during water uptake into soils, such as wetting and swelling and evaluate their environmental impact like their involvement in nutrient or contaminant distribution.

PORE SIZE DISTRIBUTION IN SOILS

It is well established that porosity and pores size distributions can be derived from relaxation time distribution of geological formations, like rocks, sandstones or permafrost and gas hydrate sediments, or materials such as ceramics (e.g. [2,

63-65]). However, even in rocks comparison of pore size distributions from different samples has to be considered carefully. The iron concentrations in rock formations are probably high enough to ensure constant surface relaxivity (compare section "water and porous media"), nevertheless, shifts in relaxation time distributions may not only be due to differences in pore size distributions, but differences in the amount of paramagnetic substances present in the sample [41, 49]. The presence of paramagnetic substances on a coated silica gel reduced the relaxation time of water close to the surface so much that the monomodal relaxation time distributions were changed to bimodal distributions, thereby identifying microporosity of the surface [49]. With increasing SOM content the number of identified water compartments increased from three to four suggesting a correlation between pore system and organic matter [52]. An even more detailed relationship between soil components and pore sizes was identified in another study: The relaxation time of soil samples was found to be dependent on sand, silt, clay and SOM content, but the degree of correlation was dependent on the pore system, i.e. micro- or mesopores. The transverse relaxation times of micropores correlate with clay and SOM contents, but those of mesopores with silt, sand and SOM [66].

In another study the influence of kaolinite addition to sandy samples was investigated [67] and found an increase in relaxation rate with increasing amount of kaolinite present in the sample. This was ascribed to the increasing surface area (increase in smaller pores) and the higher surface relaxivity of kaolinite (one reason for this higher surface relaxivity may be the presence of iron in the octahedral layers of kaolinite). However, at a certain amount of kaolinite the relaxation rate increased less. This was assumed to be the point where all sand surfaces were covered in kaolinite and the surface relaxivity was stable, leaving only decreasing pore size and changing pore geometry responsible for changes in T_1 .

A slightly different approach to determine pore mobile and immobile fractions in a wetland soil was used by Culligan *et al.* [68]: The sample (a sphagnum peat moss) was saturated with water and T_1 was determined (at 122 MHz), then a 1 mM Gd^{3+} solution was added and T_1 was determined again. As the Gd^{3+} solution was added under conditions where diffusion is negligible, this second measurement sampled only the mobile pore space. It was found that 43% of the pore space showed a fast relaxation time ($T_1 = 35$ ms), and 56% exhibited a longer relaxation time of $T_1 = 165$ ms. The first was assumed to represent the pore space filled by Gd^{3+} solution, whereas the latter only by water, therefore, confirming the existence of two porosities in the wetland peat.

One main assumption when converting relaxation time distribution into pore size distributions is that pores are not interconnected or more specific relaxation starts and ends within one pore. This may apply to geological formations which have larger pores than soils, but does not hold true for soils. Also, the pore drainage in soils can be considered to not necessarily be total, i.e. some pores drain while others retain their water [60]. Further assumptions are that the surface relaxation is constant throughout the pore system and the shape factor of the pores is constant and known [55]. In

most studies assessing pore size distributions the fast diffusion regime is assumed, so that relaxation time is influenced only by the surface relaxivity of the solid surface and the relaxation time of the bulk phase [66]. The surface relaxivity can be determined from volume to surface area ratios which in turn can be determined from e.g. nitrogen adsorption or mercury porosity measurements [55, 63, 66].

The application of NMR relaxometry to determine soil pore size distributions so far has been mainly qualitative. Several studies agree that relaxation time distributions of soil samples are related to pore sizes, but do not directly and quantitatively describe pore size distributions [53, 69]. The study conducted by Hinedi *et al.* (1993) was probably the first one to derive a real pore size distribution from a relaxation time distribution, but did not verify the outcomes by comparing them to results from conventionally obtained pore size distributions [55]. A qualitative comparison of NMR derived and conventional determined pore size distributions was undertaken in two later studies, but NMR relaxometry was recommended only as an additional method to conventional pore size determination to characterize pore connectivity [60]. However, a quantitative comparison between pore size distributions derived from NMR and conventional methods so far has been mainly conducted for several rock types [63]. Pore sizes, determined by NMR relaxation measurements in comparison to mercury porosimetry, were overestimated by an order of magnitude. Mercury porosimetry is based on the Washburn equation ($v = \frac{r\gamma_l \cos\theta}{2\eta x}$, where v is

the rate of liquid entry into the capillary, r is the capillary radius, γ_l is the liquid surface tension, η is the viscosity of the liquid, x is the distance penetrated, and θ is the contact angle [70]). It, therefore, tends to reflect more pore throats than pore sizes, leading to an underestimation of the real pore size [63]. Just recently the application of NMR relaxometry (T_2 measurements at 2 MHz) for determination of pore size distributions by quantitatively comparing it to conventional pore size distributions derived from water retention curves was verified for several soil types [66]. In this new approach, the relaxation time – pore size relation revealed two separate regions. The condition for the *fast-diffusion regime* [40] was fulfilled for $T_2 < 10$ ms. For larger T_2 values, a transition from the *fast-diffusion* to the *intermediate-diffusion regime* [40] for finer textured soil samples, and transition from the *intermediate-diffusion* to the *slow-diffusion regime* [40] for sandy soil samples was determined. Additionally, the true bulk relaxation time was used instead of the hypothetical one of free water commonly assumed for such investigations [66]. Consequently, proton relaxation in larger pores was governed by surface relaxivity and self diffusion of water. However, for simplification, the condition for the *fast-diffusion regime* was assumed as fulfilled for all pore sizes in this study. A good consistency ($R^2 = 0.98$) between pore size distributions determined by conventional soil water retention measurements and ^1H NMR relaxometry was found using the two different surface relaxivities for micro- and mesopores (for details on calculations see [66]).

As described above, the determination of conventional soil water retention curves is still necessary in order to be able to calculate surface relaxivities. In order to use the whole time-saving potential of the NMR measurements an independent method for the determination of surface relaxivities is necessary. Additionally, changes in pore sizes during water uptake as often reported have to be investigated further as they may not only be attributed to swelling of organic matter on particle surfaces or water re-distribution into pores previously not available, but also to the formation of new pore systems due to microbial activity.

COMPLEXATION OF PARAMAGNETIC IONS IN SOIL SOLUTIONS

Both relaxation times are greatly reduced in the presence of paramagnetic ions. The strength of the effect depends on the ion environment and specification. The interaction of paramagnetic ions with FA or HA in solution, thus, can be investigated using ^1H NMR relaxometry. Variations between Mn(II), Cu(II) and Fe(III) relaxation times suggested that different complexation mechanisms were at work in several studies [51, 71-73]: No change or only minimal change was found for solutions containing sulphosalicylic acid and Mn(II) in contrast to solutions with only Mn(II), suggesting the formation of outer sphere complexes, as the rotational motion of the ions was not affected [71]. However, Cu(II) and Fe(III) solutions were strongly affected by the presence of sulphosalicylic acid (reduction of relaxation time with increasing concentration of sulphosalicylic acid) suggesting the formation of inner sphere complexes [71]. Contrary findings were reported by Melton *et al.* for solutions of Laurentian HA [72]: Relaxation times of solutions with Cu(II) decreased only slightly with increasing concentration of HA [72]. The formation of stable or labile metal complexes, therefore, seems to be very dependent on the organic material. Interactions of organic compounds and FA or HA in solution were also investigated by changing concentrations and environmental parameters in the solution and their effects on relaxation times were observed. A difference in the interaction of HA and monoaromatic compounds was found depending on the aromaticity and also very strongly on pH [73]. Relaxation acceleration due to interaction with dissolved and colloidal Fe and Mn species in soil solutions causes a wide range of relaxation times in dependence of the Fe and Mn speciation [51].

FA and HA were shown to form π - π complexes with hydrophobic organic compounds like dichlorophenol. FA was less effective in forming such complexes than HA which was attributed to the stronger hydrophobic character of HA [74]. Two NMR relaxometry studies using ^{13}C -labeled acenaphthone and fluoro-acenaphthone both found evidence that the mode of interaction of FA and acenaphthone depends strongly on the concentration of FA in solution and the solution pH [75, 76].

Investigations of such interactions may help to understand the fate of organic compounds in the aquatic environment and are partly transferable to soil systems; however, the soil matrix is so much more complex and exhibits so much more opportunity for interactions apart from the soil solution, that a direct transfer is not possible.

MOBILITY AND NON-COVALENT BINDING MECHANISMS OF ORGANIC MOLECULES IN THE SOLID ORGANIC MATTER

NMR relaxometry can be used to probe the spin environment and, therefore, gain information about binding and association forms of the molecule under investigation. These investigations are indirectly related to soils as they can help predicting behaviour of organic compounds in the environment. Main constituents of SOM are fulvic acids (FA) and humic acids (HA) and several studies investigated the interaction and non-covalent binding forms of organic molecules or metal ions with HA and FA (e.g. [71, 73-79]). The identification of rigid and flexible structures within organic materials is also possible [79, 80]. The reported temperature dependence of rigid and flexible domains within HA correlated well with glass transition temperature determined by several other authors using differential scanning calorimetry (e.g. [81, 82]). Another recent study [61] reported a correlation of decrease in matrix rigidity of a peat sample with an increase of proton relaxation time (T_2). After heating a sample in an airtight container its matrix rigidity was reduced and relaxation time increased, indicating a higher mobility of the organic matter involved. After two weeks proton relaxation time had decreased to the original value and matrix rigidity increased. Suggested by earlier studies obtained from detailed DSC and TGA analysis [83-85], it was assumed that this may be due to the formation of cross-links between organic molecules *via* water molecules (physicochemical matrix aging). The thermal and moisture history is expected to be linked closely to the mobility of organics and the matrix rigidity [61]. As rigid and flexible domains probably show different sorption towards contaminants the identification and quantification of such domains within SOM is of interest for modelling contaminant sorption behaviour.

MICROBIAL INFLUENCES

Microorganisms can form extended networks, so called biofilms, in order to relieve water stress and use nutrients more efficiently. These biofilms are formed of extended extracellular polymeric substances (EPS) networks which bind water very effectively and form highly hydrated gels [86]. Biofilms or small biofilm-like structural units can also be formed in soils.

The change of the spin environment within such biofilms compared to bulk water was tested by NMR relaxation or MRI [9, 87, 88]. In aqueous solutions the monomodal relaxation time distribution (T_2 at 85 MHz) of water became bimodal in the presence of a biofilms. However, in a porous model system of glass beads the resolution of the peaks was not possible due to the relaxation effects of the solid surface of the pore system. MR images of the same samples confirmed biofilm distribution true to the optical examination [87] proving the applicability of the methods for such systems.

In soil samples the detection of biofilm growth is not that easy and bacteria do not form free biofilm inside pores, but use EPS to attach themselves to the particle surface and enhance transport of nutrients [86]. Microorganisms in soils are mainly attached to particle surfaces and primarily found in pores with diameters of 1-30 μm [89, 90].

Enhancing microorganism activity in soil samples resulted in a stronger shift of the relaxation time (T_2) towards shorter T_2 in treated (enhanced microbial activity) than untreated samples over the course of water uptake. This could be due to the increased production of EPS in the treated samples which may have reduced sizes of existing pores or formed a new micropore system. However, the contributions of other processes in reducing relaxation times like swelling of SOM or the change of surface relaxivity due to bacterial growths could not be excluded up to now [88] and further research in this area is needed.

Effects of Biofilm on Proton Relaxation Time Distributions in Model Soil Systems

In a qualitative study, the effects of bacterial biofilm on transverse relaxation time distribution of water in biofilm reactors, used as model soil systems, at 2 MHz (Maran 2, Resonance Instruments, UK) were investigated (not published). Special designed glass bottles (height x diameter: 12 cm x 5 cm; volume: 160 cm^3) with two bottle closures (at the top and bottom) were filled with glass beads of different particle sizes or with natural soil (sandy soil, sieve fraction 63 μm to 2 mm). Some of the reactors were inoculated with a biofilm producing isolate (99% sequence identity with *Sinorhizobium sp. TB8-10-II*, isolated from a waste water sand filter) and relaxation time distributions were measured after incubation time of 5 to 8 days. Optical inspection of the glass bead reactors showed biofilm growth after this time; for the soil reactor a similar growth was assumed. Fig. (2) shows the setup of the reactor system (left hand side) and a sketch of a filled reactor (right hand side). Reactors were filled with up to five layers of glass beads with particle sizes ranging from 5 mm to 150 μm (decreasing particle sizes from glass closure to bottle middle) to prevent particle outflow. Layer D in Fig. (2) represents the domain studied in the NMR relaxometer (i.e. filled with the different growing materials). 2.5 L of a 30 g L^{-1} TrypticaseTM Soy Broth solution (BD Diagnostic Systems, Heidelberg, Germany) was used as a culture medium and was pumped with 8 mL h^{-1} into a dropping funnel to prevent contamination (Fig. 2). A second pump (circulate pump with 900 mL h^{-1}) was responsible for the flow of culture medium through the reactor. After finishing the experiment, the reactors were dried using a pump. However, this was only possible for the 3 mm glass beads as the pressure was not high enough to dry the other size fractions.

¹H NMR measurements were performed using a CPMG pulse sequence [91]. The number of 180° pulses ranged between 8192 (soil) and 14336 (3 mm glass beads) with constant number of scans of 256. Echo spacing ranged between 150 μs (soil) and 300 μs (glass beads). The objective was to achieve a signal to noise ratio between 50 and 100. The repetition time was set individually for every reactor and chosen based on three to six times the longest T_2 and was 3-10 s. Relaxation time distributions were calculated from the decay curves with the WinDXP software (Resonance Instruments, UK) running a zeroth order regularisation to perform a continuous distribution of exponentials applying the BRD (Butler, Reeds and Dawson) algorithm [92]. The relaxation time distributions consisted of 128 time constants with associated amplitudes. The time constant range was 1-10000 ms, and the weight factor for the regularization was 0.5 for all biofilm reactors.

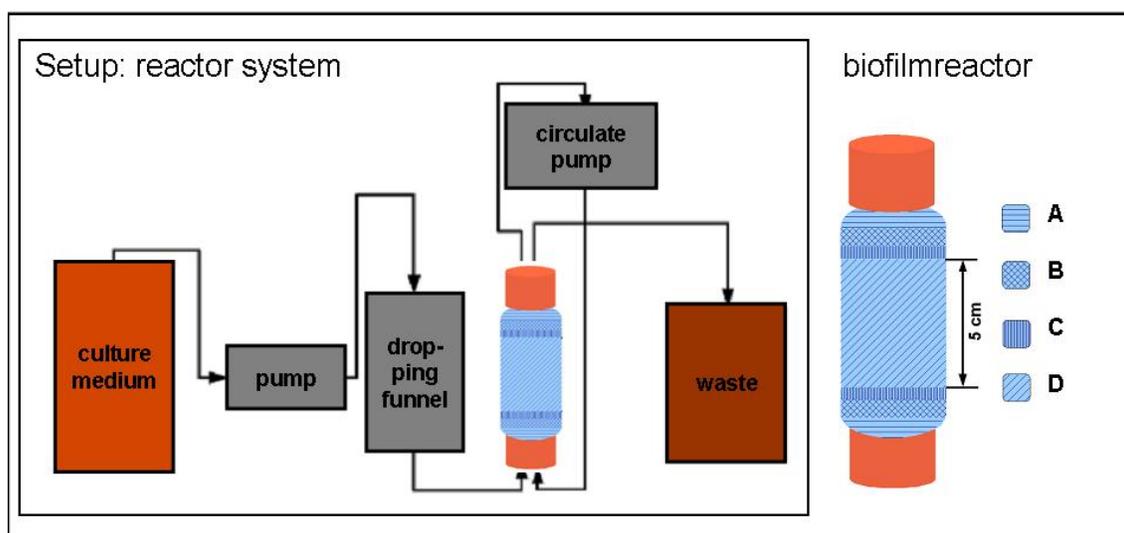


Fig. (2). Setup of the reactor system (left hand side) and a sketch of a biofilm reactor filled with glass beads (right hand side).

Transverse relaxation time distribution of water in reactors filled with 3 mm glass beads (Fig. 3) or 500-350 μm glass beads (Fig. 4) consisted of two to three peaks. Peak 0 (3 mm glass beads: $T_2 = 40\text{-}90$ ms; 500-350 μm glass beads: $T_2 = 30\text{-}40$ ms) may be a fitting artefact, because its existence and position was not reproducible in the replicate samples. Furthermore, its intensity was in the range background noise. Position of Peak 1 was $T_2 = 300$ ms for 3 mm glass beads without biofilm and up to 500 ms for 3 mm glass beads with biofilm (Fig. 3). For 500-350 μm glass beads, Peak 1 was determined around $T_2 = 150$ ms for reactors with and without biofilm (Fig. 4). This suggests that Peak 1 represents water between the contact areas of the glass particles, because its position decreased and its intensity increased with decreasing particle size in the reactors without biofilm. In the time scale of the NMR experiment, this water is not exchanging with water in larger pores as represented by Peak 2, and, thus, may be represented by an individual peak. In

the inoculated glass bead reactors, it may include water inside the biofilm matrix, because its intensity tended to increase with increasing biofilm dry mass. This suggestion is supported by the finding for agar gels, which were used as model biofilm, were T_2 ranged between 1100 ms and 100 ms for agar concentrations of 1.0-10 g L^{-1} (not shown). Peak 2 may represent water in large antiparticle pores, because its position decreased with decreasing particle size (3 mm glass beads: $T_2 = 2300$ ms without and ~ 2000 ms with biofilm; 500-350 μm glass beads: $T_2 = 1100$ ms without and ~ 800 ms with biofilm).

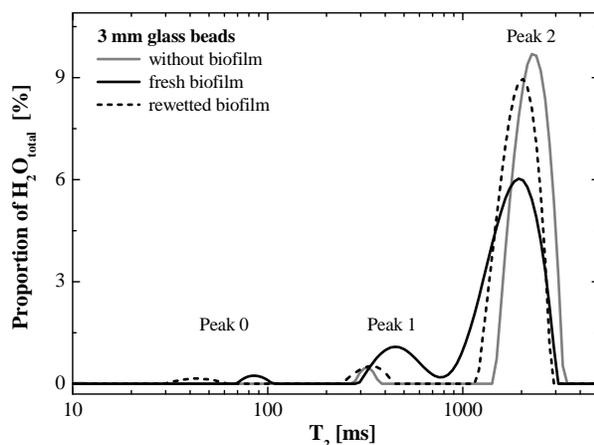


Fig. (3). Transverse relaxation time distribution of water in reactors filled with 3 mm glass beads with and without fresh biofilm, and with rewetted biofilm after air drying of the reactor with fresh biofilm.

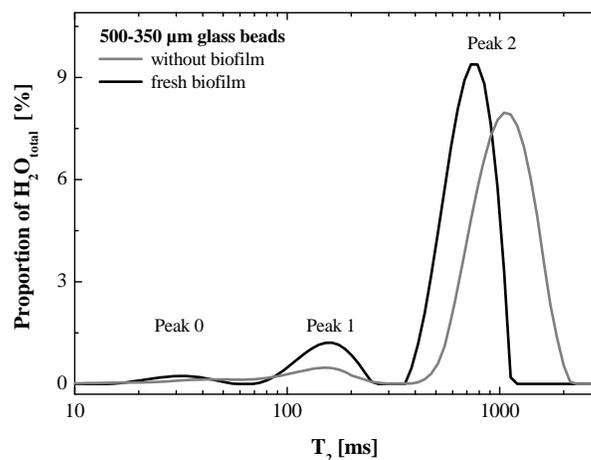


Fig. (4). Transverse relaxation time distribution of water in reactors filled with 500-350 μm glass beads with and without fresh biofilm.

For both types of glass beads, biofilm growth resulted in a shifting of peak 2 towards smaller T_2 values (Fig. 3, 4). This suggests decreasing interparticle pore diameters and/or changes of the surface relaxivity caused by biofilm on the glass bead surfaces. Additionally, the intensity of peak 1 tended to increase in the reactors with fresh biofilm. This observation was not determined for the rewetted biofilm (Fig. 3), suggesting structural changes due to drying.

The T_2 distribution of water in reactors filled with natural soil (sieve fraction 63-2000 μm) consisted of three peaks, representing water in different pore types (Fig. 5). Bacterial inoculation resulted in considerable changes of the T_2 distribution. The intensity of peak 1 increased and peak 2 and 3 showed a trend to decreasing intensity. This suggests that pore diameters of larger inter-particle pores decreased and that the amount of smaller pores increased due to the formation of biofilm inside the soil matrix. One inoculated soil filled reactor was found to be clogged and also changes in the T_2 distribution were very strongly developed (biofilm 2 in Fig. 5), suggesting a very strong biofilm growth. A clogging due to small soil particle sizes can most likely be excluded, because particles smaller 63 μm were removed by sieving prior to the experiment. Furthermore, the control reactor without inoculation showed no evidence of clogging. Biofouling and pore clogging is also known in technical applications like tubes, membrane filters and sand filters [93]. The results of the soil filled reactors are qualitatively comparable to those of Jaeger *et al.* and support their assumption that biofilm formation affected the T_2 distribution of water in soil samples with higher microbial respiratory activity [88].

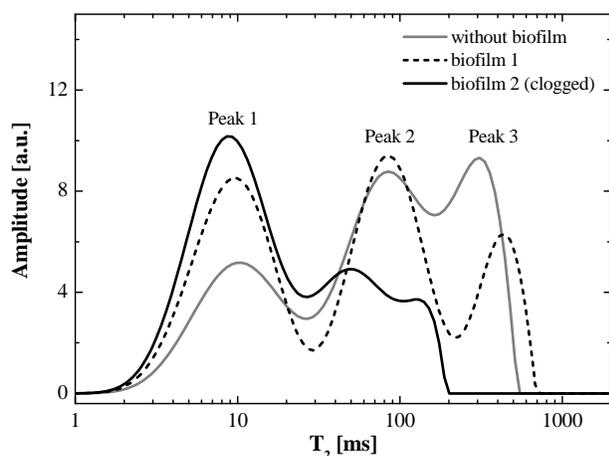


Fig. (5). Transverse relaxation time distribution of water in reactors filled with natural soil (sieve fraction 63-2000 μm) with and without fresh biofilm.

A 50 times higher transverse than longitudinal relaxivity was determined for agar gels at 30 MHz. This finding can be interpreted in terms of a reduced rotational mobility of the water molecules due to water structuring of the polymer [94]. Thus, a combination of T_1 and T_2 measurements can be suggested for a more detailed study of biofilm or other gel phases, e.g. inside the SOM matrix [54]. This may be helpful to determine different water states and to discriminate between the effects of water mobility and pore size distribution in biofilm or gel containing porous media.

OUTLOOK

The potential of proton NMR relaxometry for soil science is still far from being fully exploited. In order to utilize the full potential of the NMR technique, it is necessary to adapt it to the specific complexity and heterogeneity of soils to gain a more detailed understanding of interaction dynamics and soil-specific processes. Related NMR methods for

pore size and water distribution in soils evaluation are stray field STRAFI NMR that uses a strong magnetic field gradient in a high field superconducting magnet, as well as pulsed field gradient PFG NMR measurements for diffusion coefficients determination. The latter is especially promising in combination with NMR relaxometry [60, 64, 95, 96] to relate relaxation time with molecular diffusivity. During the last ten years mobile NMR devices have been developed in order to be able to investigate porosity and water distribution in samples *in-situ* with devices that promise easy handling. Several different approaches should be mentioned here, including the NMR MOUSE (mobile universal surface explorer) a unilateral scanner [29, 30, 35-37] and in-side-out NMR devices like the Hallbach Scanner for bore hole applications [2, 31-34]. Field cycling NMR techniques span a wide range of magnetic fields and, therefore, proton Larmor frequencies (10 kHz-40 MHz) within one single instrument. These techniques are a powerful and promising tool to study interaction dynamics [39]. Although the fields of application do not yet span investigation of soil samples, especially field cycling NMR will help to gain valuable complementary detailed understanding on interactions between soil and water.

The development of new T_1 pulse sequences reducing the overall measurement time may lead to a more frequent use of T_1 measurements. This may further improve the understanding of soil-water interactions as T_1 probes more directly interactions of the spin system (i.e. water) and the environment (i.e. the pore surface).

The potential of NMR relaxometry lies in the strong sensitivity of relaxation times to numerous factors relevant in soil-water-organics interactions, which is, however, at the same time disadvantageous and hides the danger of severe misinterpretations especially in systems as complex, versatile and heterogeneous as soils. It, thus, has to be kept in mind that conclusions on soil processes have to be drawn with care and on the basis on detailed targeted process analysis.

ABBREVIATIONS

DSC	=	differential scanning calorimetry
EPS	=	extra cellular polymeric substances
FA	=	fulvic acid
HA	=	humic acid
MOUSE	=	mobile universal surface explorer
MRI	=	magnetic resonance imaging
NMR	=	nuclear magnetic resonance
NOM	=	natural organic matter
PFG NMR	=	pulsed field gradient NMR
RF	=	radio frequency
SOM	=	soil organic matter
STRAFI NMR	=	stray field NMR

ACKNOWLEDGEMENTS

We like to thank Hella Korn, Dr. Uta Böckelmann and Daniel Wicke from the TU Berlin for their help with the biofilm reactors. This study was part of the projects

SCHA849/5 and SCHA849/8 funded by the German Research foundation (DFG).

REFERENCES

- [1] Kleinberg RL. Nuclear magnetic resonance. In: Wong P-Z, Ed. *Methods in the physics of porous media*. New York: Academic Press 1999; pp. 337-85.
- [2] Dunn K-J, Bergman DJ, Latorraca GA. *Handbook of geographic exploration-seismic exploration: nuclear magnetic resonance-petrophysical and logging applications*. Elsevier Science Ltd.: Oxford 2002.
- [3] Bluemich B. Solid-state NMR of heterogeneous materials. *Adv Mater* 1991; 3: 237-45.
- [4] Bluemler P, Bluemich B. NMR of polymers in the solid-state. *Spectrosc Eur* 1995; 7: 8-16.
- [5] Conte P, Spaccini R, Piccolo A. State of the art of CPMAS ¹³C-NMR spectroscopy applied to natural organic matter. *Prog Nucl Magn Reson Spectrosc* 2004; 44: 215-23.
- [6] Preston CM. Applications of NMR to soil organic matter analysis: history and prospects. *Soil Sci* 1996; 161: 144-66.
- [7] Randall EW, Mahieu N, Ivanova GI. NMR studies of soil, soil organic matter and nutrients: Spectroscopy and imaging. *Geoderma* 1997; 80: 307-25.
- [8] Lens PNL, Hemminga MA. Nuclear magnetic resonance in environmental engineering: principles and applications. *Biodegradation* 1998; 9: 393-409.
- [9] Lens PNL, Van AH. Use of ¹H NMR to study transport processes in biofilms. In: P.N.L. Lens, T. Mahony TM, P. Stoodley, O'Flaherty V, Eds. *Biofilms in medicine, industry and environmental biotechnology: characteristics, analysis and control* IWA Publishing, London, UK 2003; pp. 285-307.
- [10] Xiong J, Lock H, Chuang I-S, Keeler C, Maciel GE. Local motions of organic pollutants in soil components, as studied by ²H NMR. *Environ Sci Technol* 1999; 33: 2224-33.
- [11] Fomba KW. Investigation of the mobility of organic contaminants in humic substances. Leipzig: Universität Leipzig 2008.
- [12] Schaumann GE. Soil organic matter beyond molecular structure. 1. Macromolecular and supramolecular characteristics. *J Plant Nutr Soil Sci* 2006; 169: 145-56.
- [13] Schaumann GE. Soil organic matter beyond molecular structure. 2. Amorphous nature and physical aging. *J Plant Nutr Soil Sci* 2006; 169: 157-67.
- [14] Amin MHG, Richards KS, Chorley RJ, Gibbs SJ, Carpenter TA, Hall LD. Studies of soil-water transport by MRI. *Magn Reson Imaging* 1996; 14: 879-82.
- [15] Amin M, Hall LD, Chorley RJ, Carpenter TA, Richards KS, Bache BW. Magnetic resonance imaging of soil-water phenomenon. *Magn Reson Imaging* 1994; 12: 319-21.
- [16] Amin MHG, Chorley RJ, Richards KS, *et al.* STUDY of infiltration into a heterogeneous soil using magnetic resonance imaging. *Hydrol Process* 1997; 11: 471-83.
- [17] Bortolotti V, Camaiti M, Casieri C, De Luca F, Fantazzini P, Terenzi C. Water absorption kinetics in different wettability conditions studied at pore and sample scale in porous media by NMR with portable single-sided and laboratory imaging devices. *J Magn Reson* 2006; 181: 287-95.
- [18] Chen J-D, Dias MM, Patz S, Schwartz LM. Magnetic resonance imaging of immiscible-fluid displacement in porous media. *Phys Rev Lett* 1988; 61: 1489.
- [19] Davies S, Hardwick A, Roberts D, Spowage K, Packer KJ. Quantification of oil and water in preserved rock by NMR spectroscopy and imaging. *Magn Reson Imaging* 1994; 12: 349-53.
- [20] Baumann T, Petsch R, Niessner R. Direct 3-D measurement of the flow-velocity in porous media using magnetic resonance tomography. *Environ Sci Technol* 2000; 34: 4242-8.
- [21] Hall LD, Gao Amin MH, Dougherty E, *et al.* MR properties of water in saturated soils and resulting loss of MRI signal in water content detection at 2 tesla. *Geoderma* 1997; 80: 431-48.
- [22] Belliveau SM, Henselwood TL, Langford CH. Soil wetting processes studied by magnetic resonance imaging: correlated study of contaminant uptake. *Environ Sci Technol* 2000; 34: 2439-45.
- [23] Nestle N, Wunderlich A, Baumann T. MRI studies of flow and dislocation of model NAPL in saturated and unsaturated sediments. *Eur J Soil Sci* 2008; 59: 559-71.
- [24] Cheng Y, MacMillan B, MacGregor RP, Balcom BJ. Direct detection of hydrocarbon displacement in a model porous soil with magnetic resonance imaging. *Anal Chem* 2005; 77: 1824-30.
- [25] Mair RW, Hürlimann MD, Sen PN, Schwartz LM, Patz S, Walsworth RL. Tortuosity measurement and the effects of finite pulse widths on xenon gas diffusion NMR studies of porous media. *Magn Reson Imaging* 2001; 19: 345-51.
- [26] Lounila J, Telkki V-V, Jokisaari J. Extracting information on porous materials by xenon porometry. *Magn Reson Imaging* 2007; 25: 569-70.
- [27] Rubin H, Narkis N, Carberry JB. Overview of NAPL contamination and reclamation. In: Rubin H, Narkis N, Carberry JB, Eds. *Soil and aquifer pollution*. Heidelberg: Springer-Verlag 1998; pp. 3-17.
- [28] Foth HD. *Fundamentals of soil science*. 8th ed. New York: John Wiley & Sons, Inc. 1990.
- [29] Eidmann G, Savelsberg R, Bluemler P, Bluemich B. The NMR MOUSE, a mobile universal surface explorer. *J Magn Reson, Ser A* 1996; 122: 104-9.
- [30] Bluemich B, Anferova S, Pechinig R, Pape H, Arnold J, Clauser C. Mobile NMR for porosity analysis of drill core sections. *J Geophys Eng* 2004; 1: 177-80.
- [31] Anferova S, Anferov V, Rata DG, *et al.* A mobile NMR device for measurement of porosity and pore size distributions of drilled core samples. *Concepts Magn Reson Part B* 2004; 23B: 26-32.
- [32] Anferov V, Anferova S, Voda MA, Kupferschlaeger K, Blümich B. Mobile NMR scanners for nondestructive measurements of porosity of drill cores. *Magn Reson Imaging* 2007; 25: 547.
- [33] Anferova S, Anferov V, Arnold J, *et al.* Improved Halbach sensor for NMR scanning of drill cores. *Magn Reson Imaging* 2007; 25: 474-80.
- [34] Anferova S, Talmishnikh E, Anferov V, *et al.* Determination of porosity and novel 2D relaxation and diffusion experiments with mobile NMR halbach scanner. *Magn Reson Imaging* 2007; 25: 547-8.
- [35] Blümich B, Blümmler P, Eidmann G, *et al.* The NMR-mouse: construction, excitation, and applications. *Magn Reson Imaging* 1998; 16: 479-84.
- [36] Blümich B, Casanova F, Perlo J, *et al.* Advances of unilateral mobile NMR in nondestructive materials testing. *Magn Reson Imaging* 2005; 23: 197-201.
- [37] Kühn H, Klein M, Wiesmath A, *et al.* The NMR-MOUSE®: quality control of elastomers[small star, filled]. *Magn Reson Imaging* 2001; 19: 497-9.
- [38] Kleinberg RL, Straley C, Kenyon WE, Akkurt R, Farooqui SA. Nuclear Magnetic Resonance of Rocks: T₁ vs. T₂. Society of Petroleum Engineers 68th Annual Technical Conference and Exhibition of the Society of Petroleum Engineers, Houston 1993; pp. 553-63.
- [39] Kimmich R, Anardo E. Field-cycling NMR relaxometry. *Prog Nucl Magn Reson Spectrosc* 2004; 44: 257-320.
- [40] Brownstein KR, Tarr CE. Importance of classical diffusion in NMR studies of water in biological cells. *Phys Rev A* 1979; 19: 2446-53.
- [41] Godefroy S, Korb JP, Fleury M, Bryant RG. Surface nuclear magnetic relaxation and dynamics of water and oil in macroporous media. *Phys Rev E: Stat Nonlinear Soft Matter Phys* 2001; 64: 021605.
- [42] Provencher SW. A constrained regularization method for inverting data represented by linear algebraic or integral equations. *Comput Phys Commun* 1982; 27: 213-27.

- [43] Borgia GC, Brown RJS, Fantazzini P. Examples of marginal resolution of NMR relaxation peaks using UPEN and diagnostics. *Magn Reson Imaging* 2001; 19: 473-5.
- [44] Borgia GC, Brown RJS, Fantazzini P. Uniform-penalty inversion of multiexponential decay data. *J Magn Reson* 1998; 132: 65-77.
- [45] Schaumann GE, Hobley E, Hurraß J, Rotard W. H-NMR Relaxometry to monitor wetting and swelling kinetics in high organic matter soils. *Plant Soil* 2005; 275: 1-20.
- [46] Prebble RE, Currie JA. Soil water measurement by a low-resolution nuclear magnetic resonance technique. *Eur J Soil Sci* 1970; 21: 273-88.
- [47] McBrierty VJ, Wardell GE, Keely CM, O'Neill EP, Prasad M. The characterization of water in peat. *Soil Sci Soc Am J* 1996; 60: 991-1000.
- [48] Delville A, Letellier M. Structure and dynamics of simple liquids in heterogeneous condition: an NMR study of the clay-water interface. *Langmuir* 1995; 11: 1361-7.
- [49] Bryar TR, Daughney CJ, Knight RJ. Paramagnetic effects of iron(III) species on nuclear magnetic relaxation of fluid protons in porous media. *J Magn Reson* 2000; 142: 74-85.
- [50] Kenyon WE, Kolleny JA. NMR surface relaxivity of calcite with adsorbed Mn^{2+} . *J Colloid Interface Sci* 1995; 170: 502-14.
- [51] Jaeger F, Rudolph N, Lang F, Schaumann GE. Effects of soil solution's constituents on proton NMR relaxometry of soil samples. *Soil Sci Soc Am J* 2008; 72: 1694-707.
- [52] Todoruk TR, Langford CH, Kantzas A. Pore-scale redistribution of water during wetting of air-dried soils as studied by low-field NMR relaxometry. *Environ Sci Technol* 2003; 37: 2707-13.
- [53] Todoruk TR, Litvina M, Kantzas A, Langford CH. Low-field NMR relaxometry: a study of interactions of water with water-repellant soils. *Environ Sci Technol* 2003; 37: 2878-82.
- [54] Schaumann GE, Hurrass J, Müller M, Rotard W. Swelling of organic matter in soil and peat samples: insights from proton relaxation, water absorption and PAH extraction. In: Ghabbour EA, Davies G, Eds. *Humic Substances: Nature's Most Versatile Materials*. New York: Taylor and Francis, Inc., 2004: pp. 101-17.
- [55] Hinedi ZR, Kabala ZJ, Skaggs TH, Borchardt DB, Lee RWK, Chang AC. Probing soil and aquifer material porosity with nuclear magnetic resonance. *Water Resour Res* 1993; 29: 3861-6.
- [56] Hum FM, Kantzas A. Using low-field NMR to determine wettability of, and monitor fluid uptake in, coated and uncoated sands. *J Canad Petroleum Technol* 2006; 45: 23-8.
- [57] Manalo FP, Kantzas A, Langford CH. Soil wettability as determined from using low-field nuclear magnetic resonance. *Environ-SciTechnol* 2003; 37: 2701-6.
- [58] Hurrass J, Schaumann GE. Hydration kinetics of wettable and water repellent soils. *Soil Sci Soc Am J* 2007; 71: 280-8.
- [59] Ohkubo T, Kikuchi H, Yamaguchi M. An approach of NMR relaxometry for understanding water in saturated compacted bentonite. *Phys Chem Earth* 2008; 33: S169-S76.
- [60] Bird NRA, Preston AR, Randall EW, Whalley WR, Whitmore AP. Measurement of the size distribution of water-filled pores at different matric potentials by stray field nuclear magnetic resonance. *Eur J Soil Sci* 2005; 56: 135-43.
- [61] Schaumann GE, Bertmer M. Do water molecules bridge soil organic matter molecule segments? *Eur J Soil Sci* 2008; 59: 423-9.
- [62] Howard JJ. Quantitative estimates of porous media wettability from proton NMR measurements. *Magn Reson Imaging* 1998; 16: 529-33.
- [63] Liaw H-K, Kulkarni R, Chen S, Watson AT. Characterization of fluid distributions in porous media by NMR techniques. *AIChE J* 1996; 42: 538-46.
- [64] Kinchesh P, Samoilenko AA, Preston AR, Randall EW. Stray field nuclear magnetic resonance of soil water: development of a new, large probe and preliminary results. *J Environ Qual* 2002; 31: 494-9.
- [65] Kleinberg RL. Nuclear magnetic resonance pore scale investigation of permafrost and gas hydrate sediments. In: Rothwell G, Ed. *New ways of looking at sediment cores and core data*. London: Geological Society 2005: pp. 1-31.
- [66] Jaeger F, Bowe S, Van As H, Schaumann GE. Evaluation of 1H NMR relaxometry for the assessment of pore size distribution in soil samples. *Eur J Soil Sci* 2009; 60: 1052-64.
- [67] Grønras T, Rueslåtten H, Roaldset E, Skjetne T. NMR responses to kaolinite in sand. *Magn Reson Imaging* 1996; 14: 961-2.
- [68] Culligan PJ, Sinfield JV, Maas WE, Cory DG. Use of NMR relaxation times to differentiate mobile and immobile pore fractions in a wetland soil. *Water Resour Res* 2001; 37: 837-42.
- [69] Schaumann GE, Hobley E, Hurrass J, Rotard W. Changes of porosity and soil physical chemistry due to drying and re-wetting cycles. *Mitt Dtsch BodenkdL Ges* 2003; 101: 39-40.
- [70] Chibowski E, Holysz L. On the use of Washburn's equation for contact angle determination. *J Adhes Sci Technol* 1997; 11: 1289-301.
- [71] Deczky K, Langford CH. Application of water nuclear magnetic resonance relaxation times to study of metal complexes of the soluble soil organic fraction fulvic acid. *Can J Chem* 1978; 56: 1947-51.
- [72] Melton JR, Kantzas A, Langford CH. Nuclear magnetic resonance relaxometry as a spectroscopic probe of the coordination sphere of a paramagnetic metal bound to a humic acid mixture. *Anal Chim Acta* 2007; 605: 46-52.
- [73] Nanny MA, Maza JP. Noncovalent interactions between monoaromatic compounds and dissolved humic acids: a deuterium NMR T1 relaxation study. *Environ Sci Technol* 2001; 35: 379-84.
- [74] Smejkalova D, Piccolo A. Host-guest interactions between 2,4-dichlorophenol and humic substances as evaluated by 1H NMR relaxation and diffusion ordered spectroscopy. *Environ Sci Technol* 2008; 42: 8440-5.
- [75] Dixon AM, Mai MA, Larive CK. NMR investigation of the interactions between 4'-fluoro-1'-acetonephthone and the suwannee river fulvic acid. *Environ Sci Technol* 1999; 33: 958-64.
- [76] Nanny MA, Bortiatynski JM, Hatcher PG. Noncovalent interactions between acenaphthenone and dissolved fulvic acid as determined by ^{13}C NMR T1 relaxation measurements. *Environ Sci Technol* 1997; 31: 530-4.
- [77] Bryar TR, Knight RJ. Sensitivity of nuclear magnetic resonance relaxation measurements to changing soil redox conditions. *Geophys Res Lett* 2002; 29(24): 2197.
- [78] Madinelli G. NMR imaging application to the study of adsorption/precipitation of chemicals inside porous media. *Magn Reson Imaging* 1998; 16: 665-8.
- [79] Wang K, Dickinson LC, Ghabbour EA, Davies G, Xing B. Proton spin-lattice relaxation times of humic acids as determined by solution NMR. *Soil Sci* 2003; 168: 128-36.
- [80] Gunasekara AS, Simpson MI, Xing B. Identification and characterization of sorption domains in soil organic matter using structurally modified humic acids. *Environ Sci Technol* 2003; 37: 852-8.
- [81] LeBoeuf EJ, Weber Jr WJ. Macromolecular characteristics of natural organic matter. 2: sorption and desorption behavior. *Environ Sci Technol* 2000; 34: 3632-40.
- [82] Young KD, LeBoeuf EJ. Glass transition behavior in a peat humic acid and an aquatic fulvic acid. *Environ Sci Technol* 2000; 34: 4549-53.
- [83] Schaumann GE, LeBoeuf EJ. Glass transitions in peat-their relevance and the impact of water. *Environ Sci Technol* 2005; 39: 800-6.
- [84] Schaumann GE. Matrix relaxation and change of water state during hydration of peat. *Colloids Surf A* 2005; 265: 163-70.
- [85] Schaumann GE, LeBoeuf EJ, DeLapp RC, Hurrass J. Thermomechanical analysis of air-dried whole soil samples. *Thermochim Acta* 2005; 436: 83-9.
- [86] Flemming H-C, Wingender J. Extracellular polymeric substances (EPS)-the construction material for biofilms. *Vom Wasser* 2000; 94: 245-66.

- [87] Hoskins BC, Fevang L, Majors PD, Sharma MM, Georgiou G. Selective imaging of biofilms in porous media by NMR relaxation. *J Magn Reson* 1999; 139: 67-73.
- [88] Jaeger F, Grohmann E, Schaumann GE. ¹H NMR Relaxometry in natural humous soil samples: insights in microbial effects on relaxation time distributions. *Plant Soil* 2006; 280: 209-22.
- [89] Mills AL, Powelson DK. Bacterial interactions with surfaces in soils. In Fletcher M, Ed. *Molecular and ecological diversity of bacterial adhesion*. New York: Wiley-Liss, Inc. 1996; pp. 25-57.
- [90] Kirchmann H, Gerzabek MH. Relationship between soil organic matter and micropores in a long-term experiment at Ultuna, Sweden. *J Plant Nutr Soil Sci* 1999; 162: 493-8.
- [91] Meiboom S, Gill D. Modified spin-echo method for measuring nuclear relaxation times. *Rev Sci Instrum* 1958; 29: 688-91.
- [92] Butler JP, Reeds JA, Dawson SV. Estimating solutions of first kind integral equations with nonnegative constraints and optimal smoothing. *SIAM J Numer Anal* 1981; 18: 381-97.
- [93] Flemming HC, Wingender J. Relevance of microbial extracellular polymeric substances (EPSs)--Part II: Technical aspects. *Water Sci Technol* 2001; 43: 9-16.
- [94] Radosta S, Schierbaum F, Yuriev WP. Polymer-water interaction of maltodextrins. Part II: NMR study of bound water in liquid maltodextrin-water systems. *Starch-Stärke* 1989; 41: 428-30.
- [95] Preston AR, Bird NRA, Kinches P, Randall EW, Whalley WR. STRAFI-NMR studies of water transport in soil. *Magn Reson Imaging* 2001; 19: 561-3.
- [96] Vogt C, Galvosas P, Klitzsch N, Stallmach F. Self-diffusion studies of pore fluids in unconsolidated sediments by PFG NMR. *J Appl Geophys* 2002; 50: 455-67.

Received: May 04, 2009

Revised: November 17, 2009

Accepted: January 25, 2010

© Bayer *et al.*; Licensee *Bentham Open*.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.